

DIELECTRIC SATURATION IN BIOPOLYMER SOLUTIONS

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A formula for the change in electric permittivity due to an arbitrarily strong DC electric field is derived by classical statistics and shown to predict total dielectric saturation in solutions of biopolymers in simple experiments, permitting determinations of the value and sign of the electric anisotropy of macromolecules.

Consider a dilute solution of rigid biomacromolecules having electric polarizabilities α_{\parallel} parallel and α_{\perp} perpendicular to their symmetry axis, which defines the direction of the electric dipole moment μ . If the electric field measuring the electric permittivity ε of the solution acts in the same direction as a polarizing electric field of strength E sufficient for causing alignment of all the macromolecules, the change in electric permittivity is:

$$\Delta\varepsilon(E) = \frac{4\pi}{3} \varrho \left(\frac{\varepsilon_0 + 2}{3} \right)^2 \left\{ \pm 2|\alpha_{\parallel} - \alpha_{\perp}| R_{\alpha}(E) - \frac{\mu^2}{kT} R_{\mu}(E) \right\}, \quad (1)$$

ε_0 being the electric permittivity of the isotropic solvent, in which the macromolecules are immersed at number density ϱ . The electric field-dependent functions are of the form:

$$R_{\alpha}(E) = \frac{1}{2} \{ 3L_2(p, \pm q) - 1 \} + 3p \{ L_3(p, \pm q) - L_1(p, \pm q)L_2(p, \pm q) \} \\ \pm 3q \{ L_4(p, \pm q) - L_2^2(p, \pm q) \}, \quad (2)$$

$$R_{\mu}(E) = 1 + 3L_1^2(p, \pm q) - 3L_2(p, \pm q), \quad (3)$$

where $p = \mu E/kT$ is dimensionless parameter of orientation of the dipoles, and $q = |\alpha_{\parallel} - \alpha_{\perp}| E^2/2kT$ a parameter of orientation of the electric polarizability ellipsoids. At $q \neq 0$, the generalized Langevin functions are of the form:

$$L_1(p, \pm q) = \mp \frac{p}{2q} \pm \frac{e^p - e^{-p}}{4q^{1/2} I(p, \pm q)}, \\ L_2(p, \pm q) = \frac{p^2 \mp 2q}{4q^2} \pm \frac{e^p + e^{-p}}{4q^{1/2} I(p, \pm q)} - \frac{p(e^p - e^{-p})}{8q^{3/2} I(p, \pm q)},$$

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$$\begin{aligned}
 L_3(p, \pm q) &= \mp \frac{p(p^2 \mp 6q)}{8q^3} - \frac{p(e^p + e^{-p})}{8q^{3/2} I(p, \pm q)} \pm \frac{(p^2 \mp 4q + 4q^2)(e^p - e^{-p})}{16q^{3/2} I(p, \pm q)}, \\
 L_4(p, \pm q) &= \frac{p^4 + 12q(q \mp p^2)}{16q^4} \pm \frac{(p^2 \mp 6q + 4q^2)(e^p + e^{-p})}{16q^{3/2} I(p, \pm q)} - \\
 &\quad - \frac{p(p^2 + 4q^2 \mp 10q)(e^p - e^{-p})}{32q^{3/2} I(p, \pm q)},
 \end{aligned} \tag{4}$$

involving the (tabulated) integrals [1]:

$$I(p, \pm q) = \frac{1}{2} e^{\mp \left(\frac{p}{4q} + q \right)} \int_{-q^{1/2} \pm \frac{p}{2q^{1/2}}}^{q^{1/2} \pm \frac{p}{2q^{1/2}}} e^{\pm t^2} dt. \tag{5}$$

The sign “+” refers to cigar shaped macromolecules of positive anisotropy ($\alpha_{\parallel} > \alpha_{\perp}$) whereas the sign “-” to disc shaped macromolecules with negative anisotropy ($\alpha_{\parallel} < \alpha_{\perp}$).

The generalized Langevin functions L_n for purely dipolar orientation ($q = 0$) are to be found in ref. [2].

For the case when the macromolecules undergo reorientation to a not very high degree ($p \ll 1$, $q \ll 1$), the functions (2) and (3) reduce to:

$$R_{\alpha}(E) = \frac{p^2}{3} \pm \frac{2q}{5}, \quad R_{\mu}(E) = \frac{p^2}{5} \mp \frac{4q}{15} \tag{6}$$

and the variation given by Eq. (1) goes over into the well-known Langevin-Debye formula (see *e.g.* ref. [2]) defining the dependence of $\Delta\epsilon$ on the square of the field strength E . For the case when all the macromolecules undergo complete alignment in the direction of the field vector, $R_{\alpha}(\infty) = R_{\mu}(\infty) = 1$ and Eq. (1) reduces to:

$$\Delta\epsilon(\infty) = \frac{4\pi}{3} \rho \left(\frac{\epsilon_0 + 2}{3} \right)^2 \left(\pm 2|\alpha_{\parallel} - \alpha_{\perp}| - \frac{\mu^2}{kT} \right). \tag{7}$$

This result shows that, in the case of electric saturation, measurements of $\Delta\epsilon$ will permit determinations of the sign and value of the electric anisotropy of macromolecules.

Thus, in collagen solution [3] $\mu = 1.5 \times 10^4$ Debye and $\alpha_{\parallel} - \alpha_{\perp} = 3 \times 10^{-15}$ cm³. Hence, the reorientation parameters are large: $p = 0.4 E$ and $q = 0.04 E^2$. Consequently, total electric saturation can be observed even at field strengths below 30 e. s. u. Similar large saturation effects can be expected in solutions of other biopolymers (*e.g.* DNA and RNA), viruses, *etc.* [1]. Total electric saturation would require much stronger fields in solutions of smaller molecules, but this is hardly achievable as breakdown occurs about 10^3 e. s. u.

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